

TRANSITIONS BETWEEN FINE-STRUCTURE COMPONENTS  
IN RESONANCE INTERACTIONS FOR ALKALI METALS

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The cross-section has been calculated for transitions between the fine-structure components of  $^2P_{j=3/2} \rightarrow ^2P_{j=1/2}$  for sodium in the excited 3P state consequent on collision with other sodium atoms in the ground state. It is usually assumed that dipole interaction is responsible for the transition, but it is found that this interaction varies too slowly to give the observed cross-section. A result of the correct order is obtained if exchange forces are included. Levels adiabatically separated by the dipole interaction are caused to intersect by the exchange forces, so the transition occurs.

Many measurements have been reported [1, 2] for these cross-sections for P states for various pairs ( $\text{Na}^* - \text{Na}$ ,  $\text{K}^* - \text{K}$ ,  $\text{Na}^* - \text{Ar}$ ,  $\text{Na}^* - \text{K}$ ); the observed cross-sections for identical pairs ( $\text{Na}^* - \text{Na}$ ,  $\text{K}^* - \text{K}$ ) are explained as

caused by the dipole interaction  $V_d = \frac{(\vec{d}_1 \vec{d}_2) - 3(\vec{d}_1 \vec{n})(\vec{d}_2 \vec{n})}{R^3}$ , which is finite even in the first order of approximation in this case. This makes the small difference between the  $\text{Na}^*(^2P_{j=1/2}) \rightarrow \text{Na}^*(^2P_{j=3/2})$  cross-sections for  $\text{Na}^* - \text{Na}$  and  $\text{Na}^* - \text{Ar}$  rather surprising; the cross-section in the latter case is almost unaltered, although there are no dipole forces. Exchange forces have been invoked [4] to explain the result for  $\text{Na} - \text{Ar}$ ; the calculated result is of the same order as the measured one. Here I give the cross-section for  $\text{Na}^*(^2P_{j=1/2}) \rightarrow \text{Na}^*(^2P_{j=3/2})$  in  $\text{Na}^* - \text{Na}$  collisions; dipole forces do not explain the observed value, and exchange forces have to be included.

The cross-section is that for  $^2P_{j=3/2} \rightarrow ^2P_{j=1/2}$  in sodium in the 3P state on collision with Na in the S (ground) state. The transition energy is  $16 \text{ cm}^{-1} = 0.73 \times 10^{-4} \text{ a.u.}$  The nuclei are assumed to move classically along a straight line, the characteristic distance at which the transition occurs being much greater than the gas-kinetic diameter. The other atom in the collision is of no particular interest, so it is convenient to use a function of known parity in the expansion of the wave function. I use the proper functions of the electron hamiltonian  $H^e(R)$  for two atoms without spin-orbit interaction separated by a distance R. The equations for the coefficients in the expansion are solved subject to the condition that the initial wave-function is a proper function of the spin-orbit coupling operator of proper value  $E_{j=3/2}$  if the transition is  $j = 3/2 \rightarrow j = 1/2$ .

These basis functions will be the proper functions of the total spin  $S = S_1 + S_2$  (subscripts 1 and 2 refer to the two valence electrons of  $\text{Na}_2$ ), of the projection of the orbital moment M, and of the projection of the spin  $S_z$  on the molecular axis. These functions are readily constructed from the wave functions of atoms A and B if R is large:

$$\begin{aligned} {}^1\Psi_u(M) &= \frac{1}{2} \{S^A(1)P_M^B(2) + S^A(2)P_M^B(1) + S^B(1)P_M^A(2) + \\ &\quad + S^B(2)P_M^A(1)\} {}^1\chi(S_1S_2); \\ {}^3\Psi_u(M, S_z) &= \frac{1}{2} \{S^A(1)P_M^B(2) + S^B(1)P_M^A(2) - S^A(2)P_M^B(1) - \\ &\quad - S^B(2)P_M^A(1)\} {}^3\chi_{S_z}(S_1S_2); \\ {}^1\Psi_g(M, S_z) &= \frac{1}{2} \{S^A(1)P_M^B(2) - S^B(1)P_M^A(2) + S^A(2)P_M^B(1) - \\ &\quad - S^B(2)P_M^A(1)\} {}^1\chi(S_1S_2); \\ {}^3\Psi_g(M, S_z) &= \frac{1}{2} \{S^A(1)P_M^B(2) - S^B(1)P_M^A(2) - S^A(2)P_M^B(1) + \\ &\quad + S^B(2)P_M^A(1)\} {}^3\chi_{S_z}(S_1S_2), \end{aligned} \tag{1}$$

in which  $S^A(i)$  is the atomic wave function for electron i localized in atom A,  $P_M^A(i)$  is the same for the atom in the P state with projection M on the axis, and so on;  ${}^1\chi(S_1, S_2)$ ,  ${}^3\chi_{S_z}(S_1, S_2)$  are respectively the singlet and triplet spin functions for the two electrons of projection  $S_z$  on the axis.  $M = 0$  causes (1) to describe the states  ${}^1\Sigma_u^+$ ,  ${}^3\Sigma_u^+$ ,  ${}^1\Sigma_g^+$ ,  ${}^3\Sigma_g^+$

while  $M = \pm 1$  causes it to describe states  $^1\Pi_u$ ,  $^3\Pi_u$ ,  $^1\Pi_g$ ,  $^3\Pi_g$ .

The energies given by each of these functions (neglecting  $V_{LS}$ , the spin-orbit interaction) are governed by the exchange and dipole interactions for  $R$  large; the Heitler-London approximation gives

$$\begin{aligned} ^1E_u(M) &= E_0 + V_d(M) + Y_1(M) + Y_2(M); \\ ^3E_u(M) &= E_0 - V_d(M) - Y_1(M) + Y_2(M); \\ ^1E_g(M) &= E_0 - V_d(M) + Y_1(M) - Y_2(M); \\ ^3E_g(M) &= E_0 + V_d(M) - Y_1(M) - Y_2(M), \end{aligned} \quad (2)$$

in which  $Y_1$  and  $Y_2$  are exchange integrals without and with excitation transfer:

$$\begin{aligned} Y_1 &= \langle S^A(1)P^B(2) \left| -\frac{e^2}{r_{2A}} - \frac{e^2}{r_{1B}} + \frac{e^2}{R_{AB}} + \frac{e^2}{r_{12}} \right| S^A(2)P^B(1) \rangle, \\ Y_2 &= \langle S^A(1)P^B(2) \left| -\frac{e^2}{r_{2A}} - \frac{e^2}{r_{1B}} + \frac{e^2}{R_{AB}} + \frac{e^2}{r_{12}} \right| S^B(1)P^A(2) \rangle, \end{aligned} \quad (3)$$

each integral being dependent on the projection of the P state on the axis. Here the coulomb integral reduces to a dipole interaction:

$$\begin{aligned} V_d &= \langle S^A(1)P_M^B(2) \left| -\frac{(\vec{d}_1\vec{d}_2) + 3(\vec{d}_1\vec{n})(\vec{d}_2\vec{n})}{R^3} \right| P_M^A(1)S^B(2) \rangle = \\ &= \begin{cases} -d^2/R^3 & \text{when } M = \pm 1 \\ 2d^2/R^3 & \text{when } M = 0 \end{cases}, \end{aligned} \quad (4)$$

in which  $d^2 = K |\langle S(1) | \vec{r} | P_0(1) \rangle|^2$  is the dipole moment for the 3S-2P transition in Na. The oscillator strength for this [5] gives  $d = 6.22$  a.u., although (3) gives an incorrect asymptote for the exchange integrals at large distances (see [6, 7] regarding  $H_2$ , for example). The correct expressions are easily found in this case, though;  $Na^* - Na$  differs from  $H_2$  in that there is an additional quantum number not governed by the spin because the atoms are in different states; the  $\Sigma$  term thus splits into four:  $^1\Sigma_u$ ,  $^3\Sigma_u$ ,  $^1\Sigma_g$ ,  $^3\Sigma_g$ .

The splittings are readily expressed in terms of integrals over hypersurfaces (by analogy with [6]) for functions having the property that each electron is localized on a specific atom in a specific state. These functions are readily constructed;  $U_1 = \frac{1}{2} (^1\Psi_u + ^1\Psi_g + ^3\Psi_u + ^3\Psi_g)$  tends to  $S(\vec{r}_1 + \frac{\vec{R}}{2})P(\vec{r}_2 - \frac{\vec{R}}{2}) (S^A(1)P^B(2))$  when  $\vec{r}_1 \rightarrow -\frac{\vec{R}}{2}$ ;

$\vec{r}_2 - \frac{\vec{R}}{2}$  and  $U_1 \rightarrow 0$  when  $|r_1|, |r_2| \gg |R|$ . Similarly,  $U_2 = \frac{1}{2} [(^1\Psi_u + ^1\Psi_g) - (^3\Psi_u + ^3\Psi_g)] \rightarrow S^A(2)P^B(1)$  as  $\vec{r}_1 \rightarrow +\frac{\vec{R}}{2}$ ,  $\vec{r}_2 \rightarrow -\frac{\vec{R}}{2}$ , and  $U_2 \rightarrow 0$  when  $(\vec{r}_1, \vec{r}_2)$  retreats from  $(+\frac{\vec{R}}{2}, -\frac{\vec{R}}{2})$ . Finally,  $V_1 = \frac{1}{2} [(^1\Psi_u - ^1\Psi_g) - (^3\Psi_u - ^3\Psi_g)]$  tends to  $P^A(1)S^B(2)$  when  $(\vec{r}_1, \vec{r}_2) \rightarrow (-\frac{\vec{R}}{2}, \frac{\vec{R}}{2})$  and to zero when  $(\vec{r}_1, \vec{r}_2)$  retreats from  $(-\frac{\vec{R}}{2}, \frac{\vec{R}}{2})$ .

$V_2$  differs from  $V_1$  in that  $r_1$  is replaced by  $r_2$ .

Consider the integral with respect to the volume  $\lambda$  to the left of the hyperplane  $z_1 = z_2$ :

$$\begin{aligned} &\int \int_{\lambda} (^1\Psi_u + ^1\Psi_g) H (^3\Psi_u + ^3\Psi_g) d^3r_1 d^3r_2 - \int \int_{\lambda} (^3\Psi_u + ^3\Psi_g) H (^1\Psi_u + ^1\Psi_g) \times \\ &\quad \times d^3r_1 d^3r_2 = \frac{1}{2} [(^3E_u + ^3E_g) - (^1E_u + ^1E_g)] = -2Y_1. \end{aligned}$$

This integral is converted to a surface one to give

$$Y_1 = \frac{1}{2} \oint_{\vec{S}} (U_2 \vec{\nabla} U_1 - U_1 \vec{\nabla} U_2) d\vec{S} = \frac{1}{2} \oint_{\vec{S}} (V_2 \vec{\nabla} V_1 - V_1 \vec{\nabla} V_2) d\vec{S}. \quad (5)$$

Similarly,

$$Y_2 = \frac{1}{4} [(^1E_u - ^1E_g) + (^3E_u - ^3E_g)] = \oint_S (U_2 \vec{\nabla} V_2 - V_2 \vec{\nabla} U_1 + V_1 \vec{\nabla} U_2 - U_2 \vec{\nabla} V_1) d\vec{S}. \quad (6)$$

Numerical estimates are given below.

Consider the matrix elements of  $V_{LS} = A(\vec{l}_1 \vec{S}_1 + \vec{l}_2 \vec{S}_2)$  in this basis.  $A$  is related to the transition energy:  $\Delta E = 3A/2$ . Matrix elements between states differing in parity are zero, and the only nonzero elements of  $V_{LS}$  are:

$$\begin{aligned} \langle ^3\Psi_g(M, S_Z) | V_{LS} | ^3\Psi_{g(u)}(M^1, S_Z^1) \rangle &= \langle ^3\Psi_u(MS_Z) | V_{LS} | ^3\Psi_u(MS_Z) \rangle = \\ &= \frac{1}{2} A [M \delta_{MM^1} S_Z \delta_{S_Z S_Z^1} + \delta_{M, M^1-1} \delta_{S_Z, S_Z^1+1} + \delta_{M, M^1+1} \delta_{S_Z, S_Z^1-1}], \\ \langle ^1\Psi_{g(u)}(M) | V_{LS} | ^3\Psi_{g(u)}(M^1, S_Z^1) \rangle &= \langle ^3\Psi_{g(u)}(M^1, S_Z^1) | V_{LS} | ^1\Psi_{g(u)}(M) \rangle = \\ &= \frac{1}{2} A [M \delta_{MM^1} \delta_{S_Z^1, 0} + \delta_{M, M^1-1} \delta_{S_Z^1, -1} - \delta_{M, M^1+1} \delta_{S_Z^1, +1}]. \end{aligned} \quad (7)$$

The matrix is diagonal with respect to the projection of the total moment  $Y_Z = M + S_Z$ , so  $V_{LS}$  in the basis of the 12 even (odd) functions splits up into two first-order matrices ( $Y_Z = \pm 2$ ), two third-order ones (for  $Y_Z$  of +1 and -1), and two second-order ones. Then if we seek the wave function of the system in the form

$$\begin{aligned} \Psi^g(t) &= a_1^g(t) ^3\Psi_g(+1, +1) + a_2^g(t) ^3\Psi_g(-1, -1) + b_1^g(t) ^1\Psi_g(+1, 0) + \\ &+ b_2^g(t) ^3\Psi_g(0, +1) + b_3^g(t) ^3\Psi_g(+1, 0) + c_1(t) ^1\Psi_g(-1, 0) + c_2^g(t) ^3\Psi_g(0, -1) + \\ &+ c_3^g(t) ^3\Psi_g(-1, 0) + d_1^g(t) ^1\Psi_g(0, 0) + d_2 \frac{1}{\sqrt{2}} [^3\Psi_g(-1, 1) - ^3\Psi_g(+1, -1)] + \\ &+ f_1^g(t) ^3\Psi_g(0, 0) + f_2 \frac{1}{\sqrt{2}} [^3\Psi_g(-1, +1) + ^3\Psi_g(+1, -1)] \end{aligned} \quad (8)$$

and similarly for  $\Psi^u(t)$ , we get sets of equations as follows for the coefficients: first-order equations for  $a_1^u, a_2^u, a_1^g, a_2^g$ , which make no contribution to the transition;  $b_1^g, b_2^g, b_3^g$  and  $c_1^g, c_2^g, c_3^g$  satisfy a cubic system:

$$i \frac{d}{dt} \begin{pmatrix} b_1^g \\ b_2^g \\ b_3^g \end{pmatrix} = \begin{pmatrix} \frac{d^2}{R^3} + Y_{1\pi} + Y_{2\pi} & \frac{1}{2} A & -\frac{1}{2} A \\ \frac{1}{2} A & \frac{2d^2}{R^3} - Y_{1\sigma} - Y_{2\sigma} & \frac{1}{2} A \\ -\frac{1}{2} A & \frac{1}{2} A & -\frac{d^2}{R^3} - Y_{1\pi} - Y_{2\pi} \end{pmatrix} \begin{pmatrix} b_1^g \\ b_2^g \\ b_3^g \end{pmatrix}. \quad (9)$$

while for the  $b_1^u$  and  $c_1^u$ :

$$i \frac{d}{dt} \begin{pmatrix} b_1^u \\ b_2^u \\ b_3^u \end{pmatrix} = \begin{pmatrix} -\frac{d^2}{R^3} + Y_{1\pi} + Y_{2\pi} & \frac{1}{2} A & -\frac{1}{2} A \\ \frac{1}{2} A & -\frac{2d^2}{R^3} - Y_{1\sigma} + Y_{2\sigma} & \frac{1}{2} A \\ -\frac{1}{2} A & \frac{1}{2} A & \frac{d^2}{R^3} - Y_{1\pi} + Y_{2\pi} \end{pmatrix} \begin{pmatrix} b_1^u \\ b_2^u \\ b_3^u \end{pmatrix}. \quad (10)$$

Finally, the  $d_1^u, d_2^u, f_1^u, f_2^u, d_1^g, d_2^g, f_1^g, f_2^g$  satisfy a second-order system:

$$i \frac{d}{dt} \begin{pmatrix} d_1^u \\ d_2^u \end{pmatrix} = \begin{pmatrix} \frac{2d^2}{R^3} + Y_{1\sigma} + Y_{2\sigma} & \frac{1}{\sqrt{2}} A \\ \frac{1}{\sqrt{2}} A & \frac{d^2}{R^3} - Y_{1\pi} - Y_{2\pi} - \frac{1}{2} A \end{pmatrix} \begin{pmatrix} d_1^u \\ d_2^u \end{pmatrix}. \quad (11)$$

$$i \frac{d}{dt} \begin{pmatrix} f_1^u \\ f_2^u \end{pmatrix} = \begin{pmatrix} \frac{-2d^2}{R^3} - Y_{1\sigma} + Y_{2\sigma} & \frac{1}{\sqrt{2}} A \\ \frac{1}{\sqrt{2}} A & \frac{d^2}{R^3} - Y_{1\pi} + Y_{2\pi} - \frac{1}{2} A \end{pmatrix} \begin{pmatrix} f_1^u \\ f_2^u \end{pmatrix}, \quad (12)$$

$$i \frac{d}{dt} \begin{pmatrix} d_1^g \\ d_2^g \end{pmatrix} = \begin{pmatrix} \frac{-2d^2}{R^3} + Y_{1\sigma} - Y_{2\sigma} & \frac{1}{\sqrt{2}} A \\ \frac{1}{\sqrt{2}} A & \frac{-d^2}{R^3} - Y_{1\pi} - Y_{2\pi} - \frac{1}{2} A \end{pmatrix} \begin{pmatrix} d_1^g \\ d_2^g \end{pmatrix}, \quad (13)$$

$$i \frac{d}{dt} \begin{pmatrix} f_1^g \\ f_2^g \end{pmatrix} = \begin{pmatrix} \frac{2d^2}{R^3} - Y_{1\sigma} - Y_{2\sigma} & \frac{1}{\sqrt{2}} A \\ \frac{1}{\sqrt{2}} A & \frac{-d^2}{R^3} - Y_{1\pi} - Y_{2\pi} - \frac{1}{2} A \end{pmatrix} \begin{pmatrix} f_1^g \\ f_2^g \end{pmatrix}. \quad (14)$$

The probability of the  $j = 1/2 \rightarrow j = 3/2$  transition must be found by solving (9)-(14) subject to  $\Psi(t = -\infty) = \Psi_{1/2}$ , in which  $\Psi_{1/2}$  represents all possible proper functions of  $V_{LS}$  having  $E_{1/2}$  as proper value (we are concerned with the cross-section averaged over all initial states). Then this probability is governed by the action of the projection operation in state  $P_{j=3/2} \hat{O}_{3/2} = \frac{1}{\Delta E} (\hat{V}_{LS} - A)$  on  $\Psi(t = +\infty)$ . We neglect the matrix elements related to the operator for nonadiabatic

$\hbar \dot{\Psi} \frac{\partial}{\partial \Phi}$ ; the general result would otherwise be a 12th-order system. It is reasonable to neglect these elements, because  $\hbar \dot{\Psi} \approx 0.1 \times 10^{-4} \text{ a.u.} = \Delta E/7$  for distances  $R \approx 20$ , which are important for the transition.

Consider the range of distances in (9)-(14) such that  $d^3/R^3$  (dipole interaction) is of the order of  $\Delta E/2$ ; this is one of the ranges where the transition should [3] be expected. This gives  $R_0 = 50 \text{ a.u.}$ , and here  $Y_1$  and  $Y_2$  are negligibly small, so the transition probability in this range is governed solely by the dipole interaction and is of the order of  $P =$

$$= \exp(-\kappa), \text{ where } \kappa = \frac{2\pi \left( \frac{\Delta E}{2} \right)^2}{\hbar v \left( \frac{dV}{dR} \right) \Big|_{R_0}} \approx 15. \text{ This is, no transitions occur here } (P \approx 10^{-6.5}) \text{ because the dipole interac-}$$

tion varies so slowly. This would imply a cross-section  $\sigma \sim \pi R_0 \cdot P = 10^{-18} \text{ cm}^2$  if transitions occur only in this range; but this is far less than the experimental result. This estimate is confirmed by a more detailed examination of (9)-(14) by means of adiabatic perturbation theory; this shows that the motion is adiabatic up to the region where the exchange interaction becomes comparable with the dipole one. A fresh study of (9)-(14) is required for that range, because the levels may intersect. I have evaluated the exchange integrals  $Y_{1\sigma}$  and  $Y_{2\sigma}$  for this purpose; I used atomic wave functions whose asymptotes coincide with the true ones [8]:

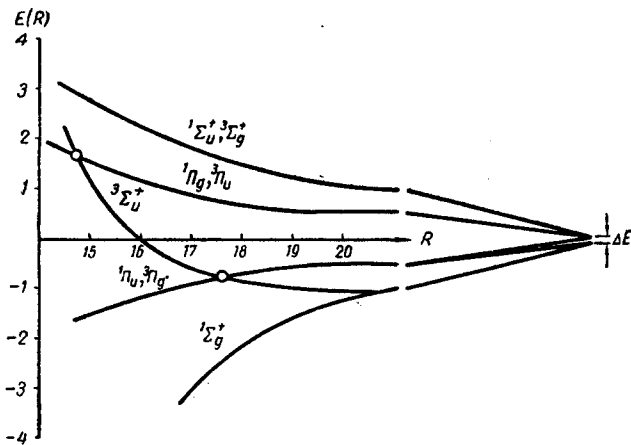
$$s(r) = \frac{c_s}{\sqrt{4\pi}} r^{\frac{1}{\alpha_s}-1} e^{-\alpha_s r}; \quad p(r) = c_p \sqrt{\frac{3}{4\pi}} \cos A e^{-\alpha_p r} r^{\frac{1}{\alpha_p}-1}, \quad (15)$$

in which  $\alpha_s = \sqrt{-2E_s} = 0.62$  and  $\alpha_p = \sqrt{-2E_p} = 0.47$  are fairly close in value;  $c_s$  and  $c_p$  may be found by comparing the functions of (15) with the Hartree-Fock ones for Na. Putting  $\alpha_s = \alpha_p = \alpha$ , we find that the asymptotes for the integrals of (5) and (6) are exactly as for  $H_2$  [6, 7] except for an extra factor  $r^{(1/\alpha)-1}$ . Calculations as in [6] give the asymptotes as

$$Y_{1\sigma} = -Y_{2\sigma} \left[ 1 + O\left( \frac{1}{(\alpha R)^2} \right) \right] = -1.7 \cdot 10^{-2} (\alpha R)^{6.5} e^{-2\alpha R} \left[ 1 + O\left( \frac{1}{\alpha^2 R^2} \right) \right]. \quad (16)$$

Also, (3) gives values fairly similar to those from (16) for  $R \approx 15$ ; similar integrals have previously been calculated [9]. In particular, (3) gives  $Y_{1\sigma}$  and  $Y_{2\sigma}$  as equal to within terms of order  $1/(\alpha R)^2$  if the  $\alpha$  are taken as equal. Also  $Y_{1\pi}$  and  $Y_{2\pi}$  are substantially less than the  $\sigma$  integrals; the figure gives a diagram of the levels on the assumptions that  $Y_{1\pi} = Y_{2\pi} = 0$  and that  $Y_1$  and  $Y_2$  are given by (16). The zero levels in (10) and (12) intersect at  $R$  of 17-18 a.u. ( $V_{LS}$  neglected), and intersection will lead to transitions between the levels consequent on spin-orbit interaction, which is nondiagonal in the original basis. The transition cross-section arising from intersection in the two sets of levels in (10) and (12) is given by the formula [10]:

$$\sigma = \pi R_0^2 2e^{-\delta} (1 - e^{-\delta}).$$



Distance  $R$  in a.u., level energies in  $10^{-3}$  a.u.

the group of states that have adiabatic transitions to a single component of the fine structure (not to different ones). Thus  $i\varphi\partial/\partial\varphi$  produces transitions only when the levels intersect. The maximal contribution from  $i\varphi\partial/\partial\varphi$  is  $\Delta\sigma_{1/2 \rightarrow 3/2} \approx 0.3 \cdot 10^{-14} \text{ cm}^2$ .

Exchange forces must therefore be considered in order to get the correct order for  $\sigma_{1/2 \rightarrow 3/2}$ ; the same is true for the  $P_{j=1/2} \rightarrow P_{j=3/2}$  transition in  $K^* - K$  collisions, because the dipole interaction alone gives a cross-section about a thousand times too small [1]. The experimental value  $\sigma_{3/2 \rightarrow 1/2} \sim 10^{-12} \text{ cm}^2$ , [11] is incorrect, because the very low pressure led to the main contribution coming from collision of  $K^*$  with the wall.

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Here  $\delta$  is  $\frac{2\pi}{4} (A)^2$   
 $\frac{\hbar v}{dR} (Y_1 - Y_2) | R_1$

about 0.2 for (12); the contribution will be  $\sigma \approx 0.5 \times 10^{-14} \text{ cm}^2$ . Other levels may intersect at smaller distances, but more detailed calculations must be made before we can say anything about this except that the cross-section could be roughly doubled. The experimental cross-section ( $1.7 \times 10^{-14} \text{ cm}^2$  [2]) agrees with this.

This neglects transitions caused by the nonadiabatic operator when levels belonging to different systems in (9)-(14) intersect;  $\hbar\varphi = \frac{1}{4} A$  for  $R \approx 15$ , and  $\hat{V} = i\varphi \frac{\partial}{\partial\varphi}$  is

easily found in the basis. This shows that transitions between levels degenerate in the zero approximation are ones within